SUBSTRATE PROCESSING APPARATUS AND SUBSTRATE PROCESSING METHOD

BACKGROUND OF THE INVENTION

Field of the Invention:

The present invention relates to a substrate processing apparatus and a substrate processing method, and more particularly to a substrate processing apparatus and a substrate processing method which are useful for removing a metal, organic materials such as a resist material and etching residues, particles, etc. adhering to a surface of a substrate, such as a semiconductor wafer.

The present invention also relates to a substrate processing apparatus, and more particularly to a substrate processing apparatus useful for carrying out wet etching by supplying a predetermined etching liquid (processing fluid) to a front surface and/or a back surface of a substrate, such as a semiconductor wafer, a glass substrate and a liquid crystal panel.

Description of the Related Art:

A high degree of cleanliness is required in a process for manufacturing a semiconductor device, and a cleaning technique for removing submicron level contamination is increasingly important. In particular, there is a demand for a new technology that can respond to new materials and processes which are becoming to be introduced into the manufacturing of a semiconductor device as semiconductor devices become finer and more highly integrated.

New materials that are becoming to be used for semiconductor devices include copper (Cu), ruthenium (Ru), cobalt (Co), platinum (Pt), etc. Of these, copper is likely to cause metal contamination. It is therefore necessary that an extra copper remaining on a substrate be completely removed. Copper is difficult to remove by a conventional RCA cleaning method, and is generally removed by using a HF-based processing liquid. Further, although most metals can be removed by a cleaning method using ozone water (O_3), it is difficult to completely remove copper.

With the trend toward semiconductor devices of finer structure, it is a recent tendency to use a low-k material as an insulating film. A new cleaning technology associated with the use of low-k material is now desired which can remove organic materials, such as polymer and etching residues, remaining on a substrate after etching of a low-k material, or can clean interiors of fine contact holes (interconnect holes) formed in the low-k material. Because of the very small diameter of fine contact holes, poor cleaning in contact holes has been a problem. In addition, because of the trend toward finer contact holes as well as the water repellency of a low-k material, cleaning of interiors of contact holes is becoming more and more difficult.

An ashing treatment using an O_2 plasma or the like can cause damage to a low-k material after formation of interconnect holes. A demand therefore exists for a new resist peeling processing that is carried out in a wet manner. Further, with the use of the above-described new materials and the progress toward finer semiconductor devices, the semiconductor device manufacturing

process itself is changing. This requires realization of a new cleaning technology that can respond to changes in the manufacturing process. For example, with the use of new resist materials and changes in etching process, there is likelihood that the adhesion of a polymer or resist residues to the underlying material, such as an insulating film, will become stronger. It is considered that such polymer or resist residues will be removed with difficulty by conventional cleaning techniques.

Further, also with respect to cleaning around gates as a pre-cleaning step, it is expected that with the progress toward finer devices and the use of new materials, removal of a metal, organic material and particles as well as prevention of re-adhesion of them after their removal will become increasingly difficult.

Wet etching of a substrate, such as a semiconductor wafer, by using an etching liquid is carried out for etching, for example, a silicon-based film, such as poly-silicon, SiO_2 or SiN, or a copper oxide film or a tantalum oxide film before electroless plating. In either case, the etching amount is required to be uniform over the substrate surface, in particular at a strict level of: $1\sigma = 1\%$ or lower.

Generally-known wet etching methods include immersion wet etching which carries out etching by immersing a substrate in an etching liquid held in an etching bath or the like, and spin etching which carries out etching by jetting an etching liquid from a spray nozzle or the like onto a substrate held in the air. With respect to the immersion wet etching, it is possible to

enhance uniformity of etching, i.e. uniformity of the etching rate, by rotating the substrate while it is kept immersed in the etching liquid. In the case of the spin etching, the uniformity of etching is known to be enhanced by rotating the substrate while a jet flow of etching liquid is supplied thereto.

In the conventional immersion wet etching, the etching liquid, held in an etching bath or the like, for immersing a substrate therein can deteriorate or change in quality with time. It is therefore necessary to manage the etching liquid in the etching bath so as to keep the liquid quality constant. The liquid management, however, is quite difficult and troublesome.

The spin etching, on the other hand, involves the following problems: When a substrate is rotated, during the supply of a jet flow of etching liquid, in order to enhance uniformity of etching, the etching liquid moves outwardly on the substrate due to centrifugal force. As the rotational speed of the substrate is increased, due to the influence of air resistance, the surface of the liquid film of etching liquid becomes wavy. This phenomenon is particularly marked in the peripheral region of the substrate with a high peripheral speed, leading to uneven etching. In particular, as shown in FIG. 19, in carrying out etching by supplying a jet flow of etching liquid Q to a substrate W while rotating the substrate W, the etching liquid Q, due to centrifugal force caused by the rotation of the substrate W, moves outwardly along the processing surface of the substrate W, with the thickness of the liquid film being minimal at the outermost peripheral portion of the substrate W. Further, since the surface of the etching liquid is in contact with the air, due

to the viscosity resistance with the air, the liquid surface becomes wavier as the peripheral speed becomes higher. A wavy liquid surface results in uneven processing, such as uneven etching, especially when the liquid film of etching liquid Q is thin. There is thus a limit in enhancing the uniformity of etching by increasing the rotational speed of the substrate.

This holds also for processing, other than etching, of a substrate such as a semiconductor wafer by immersion wet processing or spin processing using a processing fluid (processing liquid).

SUMMARY OF THE INVENTION

The present invention has been made in view of the above situation in the related art. It is therefore a first object of the present invention to provide multipurpose substrate processing apparatus and substrate processing method which can always produce a sufficient cleaning effect, responding to new materials and manufacturing processes which are becoming to be introduced into the manufacturing of semiconductor devices, and which can meet the needs for cleaning technology which are expected to increase with the progress toward finer and more highly integrated semiconductor devices.

It is a second object of the present invention to provide a substrate processing apparatus which enables relatively easy management of a processing fluid, such as an etching liquid, and which can enhance uniformity of processing, such as etching.

In order to achieve the above objects, the present invention provides a substrate processing apparatus,

comprising: a substrate holder for holding a substrate; a plurality of anodes and cathodes disposed opposite the substrate held by the substrate holder and arranged alternately along at least one direction; a processing liquid supply section for supplying a processing liquid between the substrate held by the substrate holder and the plurality of anodes and cathodes; and a power source for applying a voltage between the anodes and the cathodes.

Preferably, the substrate processing apparatus further comprises a drive mechanism for bringing the anodes and the cathodes close to the substrate held by the substrate holder, and a rotational drive mechanism for rotating the substrate held by the substrate holder.

The present invention makes it possible to provide a positive potential to a conductive material (processing object), which is formed in the surface of a substrate, through the so-called bipolar phenomenon so as to oxidize the conductive material, thereby electrically dissolving and removing the conductive material.

In a preferred embodiment of the present invention, the processing liquid contains an electrolyte.

The main purpose of the inclusion of electrolyte in the processing liquid is to impart good electrical conductivity to the processing liquid. The use as the electrolyte a halide, such as hydrogen chloride (HCl), having a strong oxidizing power, can promote oxidation of the processing object by utilizing the electrolytically dissociated halogen ion to thereby remove the object.

In a preferred embodiment of the present invention, the substrate processing apparatus further comprises a rectifier for rectifying the waveform of an electric current to be applied between the anodes and the cathodes to at least one of an alternating current waveform, a direct current waveform, a direct current reverse voltage waveform, a pulse waveform, a PR pulse waveform, and a double pulse waveform.

According to the present invention, the optimum electric current for a particular purpose can be applied between the anodes and the cathode. This enables not only oxidation of a conductive material but also removal of various processing objects present on a substrate. For example, in order to dissolve a metal formed in the surface of a substrate by utilizing the bipolar phenomenon, a direct current waveform is selected. For removal of particles, not the bipolar phenomenon but the electric mobility of an ionic surfactant is utilized, and therefore a pulse waveform or a PR pulse waveform is selected. When it is necessary to put the surface of a substrate in a reducing atmosphere, a reverse voltage waveform of a direct or pulse current is selected. Further, for the purpose of making the molecular structure of water finer in order to increase the permeability of the processing liquid, a pulse waveform having a short wavelength of microsecond (μs) order is selected.

In a preferred embodiment of the present invention, the anodes are arranged over a plane at regular intervals along orthogonal directions, and each cathode is disposed approximately in the center between two anodes adjacent to each other in an oblique direction.

In a preferred embodiment of the present invention, the cathodes are arranged over a plane at regular intervals along orthogonal directions, and each anode is disposed approximately in the center between two cathodes adjacent to each other in an oblique direction.

The present invention enables uniform processing over the entire surface of a substrate.

In a preferred embodiment of the present invention, at least one of the anodes and the cathodes are made of a conductive diamond or lead dioxide.

Platinum (Pt) is often used as an insoluble electrode in a common substrate processing apparatus. Though platinum produces O_2 through its catalytic reaction, it does not produce O_3. The use of a conductive diamond, instead of platinum, can increase the oxygen overvoltage (voltage at which O_2 begins to be generated at the anode), enabling generation of O_3. Also with lead dioxide, if used solely as an anode, an oxygen overvoltage sufficient for generation of O_3 can be obtained. Thus, according to the present invention, not only O_2 but also O_3 can also be generated at the insoluble anodes upon electrolysis of water present as a solvent in the processing liquid. It therefore becomes possible to decompose and remove etching residues and a resist material, such as a polymer, by utilizing the strong oxidizing power of O_3.

In a preferred embodiment of the present invention, the distance between the substrate held by the substrate holder and the anodes differs from the distance between the substrate held by the substrate holder and the cathodes.

According to the present invention, the oxidizing or reducing power of a gas, generated at the electrode portion which is nearer to the substrate, can be exerted on the processing liquid present in the vicinity of the surface of the substrate, thus enhancing the processing object removing effect. Further, by applying a voltage, whose polarity is reversed periodically, between the electrodes, the potential change at the substrate surface can be made larger. This promotes removal of a processing object, such as particles, electrostatically adhering to the substrate. Moreover, the molecular structure of water, present as a solvent in the processing liquid, can be made smaller so that the processing liquid can better permeate into fine contact holes, thereby effecting good cleaning.

A conventional ozone water production apparatus which has hitherto been employed is generally installed separately from the main body of a cleaning apparatus. Accordingly, there is a case where during transport of ozone water through a pipe to the location of a substrate within the cleaning apparatus, the ozone in the ozone water decomposes, failing in obtaining a uniform ozone concentration.

An electrolytically ionized water production apparatus is also generally installed independently. There is therefore a case where reactive ions, dissociated ions having a high electrical mobility, and a solvent having a minute molecular structure, which have been produced by electrolysis, cannot be maintained as they are until they reach onto a substrate.

According to the present invention, the electrolytic reaction or generation of ozone takes place in the very vicinity

of the substrate. This allows various products and ozone produced by electrolysis to act effectively. Further, the rate of oxidation reaction of ozone, which is relatively low solely with ozone, can be increased by the aid of electrical energy application.

In a preferred embodiment of the present invention, a supply port of the processing liquid supply section is provided in one of each anode and each cathode, and a suction port for sucking in the processing liquid supplied from the supply port is provided in the other one of each anode and each cathode.

The present invention also provides a substrate processing method, comprising: bringing a plurality of anodes and cathodes close to a substrate; supplying a processing liquid between the substrate and the plurality of anodes and cathodes; and applying a voltage between the anodes and the cathodes.

The present invention further provides another substrate processing apparatus, comprising: a substrate holder for holding a substrate; a processing head disposed such that it faces the substrate held by the substrate holder; and a processing liquid supply section for supplying a processing liquid between the substrate held by the substrate holder and the processing head; wherein a plurality of anodes and cathodes, and an ultrasonic transducer for emitting ultrasonic waves toward the processing liquid are disposed in the substrate-facing surface of the processing head.

In a preferred embodiment of the present invention, the substrate processing apparatus further comprises a relative movement mechanism for moving the processing head relative to

the substrate.

In a preferred embodiment of the present invention, the relative movement mechanism rotates the processing head.

In a preferred embodiment of the present invention, the substrate processing apparatus further comprises a pulse power source for applying a pulse voltage between the anodes and the cathodes.

The present invention makes it possible to provide a positive potential to a conductive material (processing object), which is present in the surface of a substrate, through the so-called bipolar phenomenon so as to oxidize the conductive material, thereby electrically dissolving and removing the conductive material. Further according to the present invention, if a conductive material is not present in the surface of a substrate, non-conductive particles, an organic material, etc. adhering to the substrate can be cleaned off effectively by emitting ultrasonic waves onto gas bubbles, such as oxygen gas or ozone gas, generated at the anodes during processing. The principle of the present invention will now be described.

When a voltage is applied between an anode and a cathode, oxygen gas or ozone gas is generated at the anode and remains as gas bubbles in a processing liquid. Such gas bubbles can be made fine by applying a pulse voltage between the anode and the cathode, or by adding a surfactant to the processing liquid.

Gas bubbles having a diameter of not more than 20 μm, in particular 1 to 10 μm, have the following characteristics:

(1) Such gas bubbles do not coalesce with one another, and they remain as independent gas bubbles in a liquid for a long

time without disappearing.

(2) The rising speed of gas bubbles is slow. The gas bubbles, therefore, show good diffusion in a horizontal direction and easily disperse uniformly in a liquid.

(3) In addition to the long residence in a liquid, the number of gas bubbles per unit volume of liquid (gas bubble content) has increased, and therefore the surfaces area of gas bubbles per unit volume of liquid has become larger. The gas bubble content increases as the gas bubbles become finer.

(4) Since the gas bubbles are electrically charged, they have adhesion to suspended solids in a liquid.

(5) Depending upon the surface tensions of the gas bubbles, the surfaces of gas bubbles reflect ultrasonic waves.

In order to effectively utilize fine bubbles (hereinafter referred to as "microbubbles") having the above characteristics in cleaning of a substrate, according to the present invention, ultrasonic waves are applied intermittently to such microbubbles in a processing liquid. The application of ultrasonic waves to microbubbles produces the following effects:

(i) Microbubbles are collapsed upon the application of ultrasonic waves, producing micro jet flows in a processing liquid. Particles, etc. adhering to a substrate can be removed by utilizing the energy of the micro jet flows. Further, when microbubbles are collapsed, the gas forming the microbubbles is dissolved at a high concentration in the processing liquid. Thus, a metal or organic material adhering to the substrate can be removed by utilizing the chemical properties of the gas.

(ii) In the case where the surface tensions of microbubbles

are strong, the bubbles are not destroyed, and are stirred by ultrasonic waves. Accordingly, the microbubbles can be diffused widely in a processing liquid, enabling particles, etc. to be adsorbed on the surfaces of microbubbles.

(iii) Ultrasonic waves are reflected diffusely on the surfaces of microbubbles, whereby ultrasonic waves can be applied also to fine processing portions, such as contact holes, formed in the surface of a substrate. This enables removal of particles, etc. adhering to the fine processing portions.

(iv) In the case of cavitation microbubbles produced by cavitation phenomenon, which could occur by application of ultrasonic waves, the impulse upon their collapse is likely to cause damage to a device. According to the present invention, the application of ultrasonic energy does not produce microbubbles. It is therefore possible to set the frequency of ultrasonic waves within such a range as not to cause damage to a device.

The present invention further provides yet another substrate processing apparatus, comprising: a processing liquid supply section for supplying a processing liquid onto a substrate; a microbubble generator for generating microbubbles in the processing liquid; and an ultrasonic transducer for emitting ultrasonic waves to the processing liquid containing microbubbles.

In a preferred embodiment of the present invention, the microbubbles have a diameter of not more than 20 μm, and have an internal pressure of not lower than atmospheric pressure.

In a preferred embodiment of the present invention, the

microbubble generator comprises a two-fluid nozzle, a gas diffuser, a gas/liquid stirrer, or an electrolytic gas generator.

In a preferred embodiment of the present invention, the substrate processing apparatus further comprises a substrate holder for holding a substrate, and a rotating mechanism for rotating the substrate, and the ultrasonic transducer is disposed such that it faces the substrate held by the substrate holder.

In a preferred embodiment of the present invention, the ultrasonic transducer has a processing liquid introduction port, and the processing liquid is supplied through the processing liquid introduction port to between the substrate held by the substrate holder and the ultrasonic transducer.

In a preferred embodiment of the present invention, the frequency of the ultrasonic waves emitted from the ultrasonic transducer is 5 to 100 MHz.

The substrate processing apparatus according to the present invention does not utilize ultrasonic application to generate microbubbles by the cavitation phenomenon, but applies ultrasonic waves to microbubbles generated by the microbubble generator. The application of ultrasonic waves to the processing liquid containing microbubbles according to the present invention can enhance the cleaning effect that microbubbles originally have. Further, by the synergistic effect of microbubbles and ultrasonic application, various processing objects, such as particles, a metal, an organic material, etc., can be removed from a substrate with a high

efficiency.

The present invention further provides yet another substrate processing apparatus, comprising: a substrate holder for holding and rotating a substrate; a rotatable rotary plate disposed opposite to one of the front and back surfaces of the substrate held by the substrate holder at a predetermined distance therefrom; and a first fluid supply section for supplying a first fluid between the substrate held by the substrate holder and the rotary plate.

The substrate processing apparatus, in principle, performs spin processing by supplying the first processing fluid, such as an etching liquid, from the first fluid supply section to the rotating substrate held by the substrate holder. By holding the processing fluid, supplied from the first fluid supply section, between the substrate held by the substrate holder and the rotary plate and preventing contact between the processing fluid and air as much as possible, uneven processing in the peripheral region of the substrate can be avoided even when the rotational speed of the substrate is high. Further, by producing the effect of rotation of substrate in immersion processing also in the spin processing, uniformity of processing, such as etching, of the substrate can be enhanced.

Preferably, the substrate holder and the rotary plate rotate in opposite directions.

This increases the relative movement speed between the substrate held by the substrate holder and the substrate, thereby enhancing uniformity of the diffusion layer on the processing surface of the substrate. From the viewpoint of preventing

damage to the substrate, it is preferred to use a low rotational speed for the substrate and a high rotational speed for the rotary plate.

The first processing fluid is, for example, an etching liquid.

In a preferred embodiment of the present invention, the substrate processing apparatus further comprises a counter plate disposed opposite to the other one of the front and back surfaces of the substrate held by the substrate holder at a predetermined distance therefrom, and a second fluid supply section for supplying a second processing fluid between the substrate held by the substrate holder and the counter plate.

The apparatus of this embodiment can simultaneously process both the front and back surfaces of the substrate held by the substrate holder with the first and second processing fluids, or can utilize the second processing fluid to prevent the first processing fluid from intruding over the peripheral end of the substrate into the non-processing surface.

The second processing fluid is, for example, a gas.

By using, for example, dry air as the second processing fluid, the first processing fluid can be prevented from intruding over the peripheral end of the substrate into the non-processing surface.

The counter plate preferably is rotatable.

This enables simultaneous processing, such as etching, of both the front and back surfaces of the substrate held by the substrate holder with improved uniformity of processing.

It is preferred that the counter plate rotates in a

direction opposite to the rotating direction of the substrate holder.

This increases the relative movement speed between the substrate held by the substrate holder and the counter plate.

The second processing fluid may also be an etching liquid.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a cross-sectional view showing the overall construction of a substrate processing apparatus according to an embodiment of the present invention;

FIG. 2 is a schematic plan view of the substrate processing apparatus shown in FIG. 1;

FIG. 3 is a cross-sectional view of the processing head shown in FIG. 1;

FIG. 4 shows the processing head of FIG. 3 as viewed in the direction of arrow B;

FIG. 5A is an enlarged sectional view of the anode and the cathode shown in FIG. 3, and FIG. 5B is an enlarged section view of other anode and cathode;

FIG. 6A is a diagram showing a PR pulse waveform, FIG. 6B is a cross-sectional diagram illustrating the function of the anode and the cathode during the interval "a" shown in FIG. 6A, and FIG. 6C is a cross-sectional diagram illustrating the function of the anode and the cathode during the interval "b" shown in FIG. 6A;

FIG. 7 is an enlarged sectional diagram illustrating the progress of electrolytic processing as performed by the substrate processing apparatus according to the present

invention;

FIG. 8 is a cross-sectional view showing the processing head when the anodes and the cathodes are reversed;

FIG. 9 is a plan view showing the construction of a substrate processing system provided with a substrate processing apparatus according to the present invention;

FIG. 10 is a cross-sectional view showing the overall construction of a substrate processing apparatus according to another embodiment of the present invention;

FIG. 11 is a view showing the lower surface of the processing head shown in FIG. 10;

FIG. 12 is a cross-sectional view taken along the line IV-IV of FIG. 11;

FIG. 13 is a cross-sectional view showing the overall construction of a substrate processing apparatus according to yet another embodiment of the present invention;

FIG. 14 is a schematic diagram showing a substrate processing apparatus, which is utilized as an etching apparatus, according to yet another embodiment of the present invention;

FIG. 15A is an enlarged view of the main portion of FIG. 14, and FIG. 15B shows a variation thereof;

FIG. 16 is a schematic diagram showing a substrate processing apparatus, which is utilized as an etching apparatus, according to yet another embodiment of the present invention;

FIG. 17 is a schematic diagram showing a substrate processing apparatus, which is utilized as an etching apparatus, according to yet another embodiment of the present invention;

FIG. 18 is a plan view showing the construction of a

substrate processing system provided with an etching apparatus (substrate processing apparatus) according to the present invention; and

FIG. 19 is a diagram illustrating a problem that a conventional spin etching has.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

Preferred embodiments of the present invention will now be described with reference to the drawings.

FIG. 1 is a cross-sectional view showing the overall construction of a substrate processing apparatus according to an embodiment of the present invention. FIG. 2 is a schematic plan view of the substrate processing apparatus shown in FIG. 1.

As shown in FIG. 1, the substrate processing apparatus includes a substrate holder 3 for holding a substrate W, such as a semiconductor wafer, a main shaft 4 coupled to the lower portion of the substrate holder 4, and a vessel 5 disposed below the substrate holder 3. The main shaft 4 is rotatably supported by a not-shown bearing, and the substrate holder 3 rotates together with the main shaft 4.

The substrate holder 3 includes a circular substrate stage 6 and a plurality of support pins 7 provided on the upper surface of the substrate stage 6. The support pins 7 are arranged at regular intervals along the circumferential direction of the substrate W so that the peripheral portion of the substrate W is supported by the support pins 7. Instead of the support pins 7, a holding mechanism such as a vacuum chuck or an electrostatic

chuck may be used to hold the substrate. A rotating motor 8 is coupled to the lower end of the main shaft 4. The substrate W held by the substrate holder 3 is rotated by the rotating motor 8 via the main shaft 4.

The substrate processing apparatus of this embodiment also includes an arm 11 which is vertically movable and horizontally reciprocatable, and a processing head 12 fixed to the end of the arm 11. A reciprocating motor 14 is coupled via a power transmission mechanism 13 to the shaft portion 11a of the arm 11, so that the processing head 12 pivots in the direction of arrow A shown in FIG. 2 by the reciprocating motor 14. An air cylinder 16 is coupled to the lower end of the shaft portion 11a of the arm 11. The air cylinder 16 is connected to a not-shown compressed air source, and is driven by compressed air supplied from the compressed air source. Thus, the processing head 12 moves vertically via the shaft portion 11a and the arm 11 by the air cylinder 16. The processing head 12 can be lowered to a position at which the distance between the surface of the substrate W held by the substrate holder 3 and the lower surface of the processing head 12 is about 1 mm.

Next, the construction of the above-described processing head 12 will now be described in detail by referring to FIGS. 3 and 4. FIG. 3 is a cross-sectional view of the processing head 12 shown in FIG. 1, and FIG. 4 shows the processing head 12 of FIG. 3 as viewed in the direction of arrow B.

As shown in FIGS. 3 and 4, the processing head 12 is provided with a plurality of anodes 21 and cathodes 22. The anodes 21 and the cathodes 22 are provided in the lower surface of the

processing head 12 and are respectively arranged regularly in a predetermined pattern.

As shown in FIG. 4, the cathodes 22 are arranged over almost the entire lower surface of the processing head 12 at regular intervals along orthogonal directions. Each anode 21 is disposed in the center between two cathodes 22 adjacent to each other in an oblique direction. The anodes 21 and the cathodes 22 are thus respectively arranged in a checkered pattern in the lower surface of the processing head 12.

As shown in FIGS. 3 and 4, the cathodes 22 are provided in the interior of projecting portions 12a, each having a rectangular cross-section and projecting downwardly, of the processing head 12, while the anodes 21 are provided in grooves 12b formed between the projecting portions 12a and extending rectangularly. With such a construction, there is provided a level difference D of e.g. α mm between the anodes 21 and the cathodes 22. Thus, when the distance S_1 between the upper surface of the substrate W held by the substrate holder 3 and the cathodes 22 is about 1 mm, the distance S_2 between the anodes 21 and the upper surface of the substrate W is about $(1+\alpha)$ mm.

The cathodes 22 each have a supply port 25 that centrally penetrates the cathode 22. The supply ports 25 are connected via a pipe 26 to a processing liquid supply source 27 in which a processing liquid 2 is stored. The processing liquid 2 is supplied through the pipe 26 and the supply ports 25 onto the upper surface of the substrate W. The anodes 21 each have a suction port 29, centrally penetrating the anode 21, which is connected via a pipe 28 to a suction source (not shown). The

processing liquid 2 supplied to the upper surface of the substrate W is sucked from the suction ports 29 by the suction source and discharged out of the system. The supply port 25 may be provided in a peripheral portion of the cathode 22, and likewise, the suction port 29 may be provided in a peripheral portion of the anode 21. As shown in FIG. 3, the processing liquid 2 supplied onto the upper surface of the substrate W remains on the substrate W by the action of surface tension. Part of the processing liquid 2, however, flows out of the substrate W. The processing liquid 2 that has flowed out of the substrate W is recovered by the vessel 5 provided below the substrate holder 3.

A description will now be made of the flow of processing liquid 2 by referring to FIGS. 5A and 5B.

FIG. 5A is an enlarged sectional view of the anode 21 and the cathode 22 shown in FIG. 3, and FIG. 5B is an enlarged sectional view showing other anode 21 and cathode 22. According to the example shown in FIG. 5B, the supply port 25 is provided in the peripheral portion of the cathode 22, and the suction port 29 is provided in the peripheral portion of the anode 21. The arrows shown in FIGS. 5A and 5B indicate the flow of processing liquid 2.

As shown in FIGS. 5A and 5B, the processing liquid 2 is supplied from the supply port 25 provided in the cathode 22 onto the upper surface of the substrate W and, after flowing on the upper surface of the substrate, sucked from the suction port 29 provided in the anode 21. Thus, whether the supply port 25 and the suction port 29 are provided in the central portions or in the peripheral portions of the electrodes, the processing liquid

2 flows from the supply port 25 to the suction port 29 via the upper surface of the substrate W in substantially the same flow.

The processing liquid used in the substrate processing apparatus basically comprises a solvent such as water (ultrapure water) or an alcohol, an electrolyte such as HCl or NH_3OH, and an additive such as an ionic surfactant. The main purpose of the inclusion of an electrolyte in the processing liquid is to impart electrical conductivity to the processing liquid. Further, the use of an electrolyte enables adjustment of the liquid pH, which can produce the effect of promoting the removal of a processing object. In particular, a decrease in the pH raises the oxidation-reduction potential, whereby a strong oxidizing power can be obtained. On the other hand, by increasing the pH and making the processing liquid alkaline, the zeta potential, which is a factor of adhesion of particles to a substrate, can be lowered whereby particles can be removed effectively. When a halide, such as HCl, having a strong oxidizing power is used as the electrolyte, the halide is partly ionized into halogen ions in the processing liquid, and the halide ions can react with and oxidize a processing object to be removed.

The anodes 21 are electrically connected via a wire 31 to the anode of a power source 32, while the cathodes 22 are electrically connected via a wire 33 to the cathode of the power source 32. A conductive diamond is preferably used as a material for the anodes 21 and the cathodes 22. It is also possible to use, instead of the conductive diamond, lead dioxide (PbO_2), platinum (Pt), or the like. Except the case of electrodes made of lead dioxide, the anodes can be made cathodes and the cathodes

can be made anodes by reversing the anode and the cathode of the power source 32.

The power source 32 is provided with a rectifier 34 for rectifying the current waveform to a predetermined one. The rectifier 34 can rectify the current waveform to be outputted from the power source 32 to an alternating current waveform, a direct current waveform, a direct current reversed voltage waveform (direct current waveform with reversed polarity), a pulse waveform, a PR pulse waveform, or a double pulse waveform. The rectifier 34 can also change the frequency and the wavelength of such a waveform. The pulse waveform is not limited to a sine curve, or a triangular, rectangular or square waveform. A combination of two or more of them may also be employed.

FIG. 6A is a diagram showing a PR pulse waveform. FIG. 6B is a cross-sectional diagram illustrating the function of the anode and the cathode during the interval "a" shown in FIG. 6A, and FIG. 6C is a cross-sectional diagram illustrating the function of the anode and the cathode during the interval "b" shown in FIG. 6A. In FIG. 6A, the abscissa represents time (t) and the ordinate represents the intensity of electric current (A).

As shown in FIG. 6A, the direction of an electric current having a PR pulse waveform changes periodically. Thus, as shown in FIG. 6B, the cathode 22 becomes an anode and the anode 21 becomes a cathode during the interval "a". During the interval "b", on the other hand, the cathode 22 functions as it is as a cathode, while the anode 21 functions as it is as an anode, as shown in FIG. 6C.

The waveform, frequency and wavelength of electric current may be appropriately selected depending upon the processing object. For example, in order to dissolve a metal formed on the surface of the substrate W, a direct current waveform is selected. A direct current reverse voltage waveform is selected to remove a resist material adhering to a metal surface. A pulse waveform or a PR pulse waveform is selected for removal of particles. Further, for the purpose of making finer the molecular structure of water in the processing liquid, a pulse waveform having a short wavelength of microsecond (μs) order is selected. Thus, according to the substrate processing apparatus of this embodiment, the optimum electric current for a particular purpose can be applied between the anodes 21 and the cathodes 22. This makes it possible to remove various processing objects present on the substrate W.

The operation of the substrate processing apparatus having the above-described construction will now be described. In this embodiment, the processing object to be removed is copper (Cu) formed in the surface of the substrate W.

First, the substrate W is held by the substrate holder 3 such that the front surface (processing surface) in which copper is formed faces upwardly. The reciprocating motor 14 is driven to move the processing head 2 to above the substrate W, and the air cylinder 16 is then activated to lower the processing head 12. The lowering of the processing head 12 is stopped at a position where the distance S_1 between the lower surface of the processing head 12 and the upper surface of the substrate W held by the substrate holder 3 is about 1 mm. The rotating motor 8

is then driven to rotate the substrate W and, at the same time, the reciprocating motor 14 is driven to pivot the processing head 12.

The processing liquid 2 stored in the processing liquid supply source 27 is supplied from the supply ports 25 onto the upper surface of the substrate W, while the processing liquid 2 on the substrate W is sucked from the suction ports 29. A predetermined voltage is applied from the power source 32 to between the anodes 21 and the cathodes 22, whereby electrolytic processing (electrolytic etching) proceeds. The current waveform outputted from the power source 32 is selected depending upon the processing object, and a direct current waveform is selected in this embodiment.

FIG. 7 is an enlarged sectional diagram illustrating the progress of electrolytic processing, which removes copper as a bulk metal or as a metal contaminant from the substrate, as performed by the substrate processing apparatus of this embodiment. As shown in FIG. 7, when a voltage is applied between the anodes 21 and the cathodes 22 in the presence of the processing liquid 2 containing an electrolyte, the portion of copper 50 close to the anode 21 takes on a negative potential while the portion of copper 50 close to the cathode 22 takes on a positive potential. This phenomenon is called bipolar phenomenon. Copper oxidation reaction ($Cu \rightarrow Cu^{2+} + 2e^-$) occurs at the portion of copper 50 with a positive potential, while H_2 generation occurs at the portion of copper with a negative potential. A potential difference is thus produced within copper 50, causing migration of electrons (e^-). In this manner, electrolytic processing

(electrolytic etching) proceeds at the positively charged portion of copper 50 whereby the copper 50 to be processed is dissolved.

The processing liquid 2 supplied to the upper surface of the substrate W flows on the upper surface of the substrate, and is then sucked from each suction port 29 and continuously discharged out of the system. Part of the processing liquid 2 falls off the surface of the substrate W, which liquid is recovered in the vessel 5 provided below the substrate holder 3. Though in this embodiment the processing head 12 is pivoted by the reciprocating motor 14 during electrolytic processing, it is also possible to allow the processing head 12 to make a scroll movement instead of the pivoting movement.

In electrolytic processing for dissolving a metal, the current waveform outputted from the power source 32 is set to a direct current waveform, and the output voltage of the power source 32 is set at 10 to 100 V. The electric resistivity between the anode 21 and the cathode 22 is preferably from 5 to 50 Ω·cm.

A description will now be given of removal of an organic material, such as a polymer or a resist material, adhering to the surface of the substrate W by the substrate processing apparatus of this embodiment by referring to FIG. 8. As shown in FIG. 8, in removing an organic material, such as a polymer or a resist material, by using the substrate processing apparatus of this embodiment, the substrate surface needs a high oxidizing power and a reaction promoting energy. In this case, the electrodes closer to the substrate W are made anodes 21 and the electrodes farther from the substrate W are made cathodes 22.

A conductive diamond is preferably used as a material for the anodes 21 for the following reasons. The voltage at which O_2 begins to be generated at the anodes 21 (hereinafter referred to as oxygen overvoltage) depends on the degree of catalytic activity of the material of the anodes 21. The oxygen overvoltage increases in the following order: platinum (Pt) < lead dioxide (PbO_2) < diamond. Accordingly, the use of a conductive diamond as a material for the anodes 21 suppresses the generation of O_2 at the anodes 21 and increases the ratio of O_3 generation.

In general, ozone water (O_3) may be used for removal of a polymer or a resist material adhering to a substrate W. A conventional ozone water production apparatus of a stand-alone type has the problem that the O_3 concentration of ozone water decreases during its transfer to the substrate W, whereby the desired oxidizing power cannot be obtained.

According to this embodiment, by using a conductive diamond as a material for the anodes 21, O_3 can be generated at the very vicinity of the substrate W. This makes it possible to effectively utilize the oxidizing power of O_3 in removing an organic material, such as a polymer or a resist material. It is also possible to utilize the oxidizing power of active oxygen species, such as O, O_2^- and O_3^-, generated at the anodes 21. By utilizing an electrical energy, such as of a pulse waveform, or the effect of an electrolyte so as to increase the reaction rate of O_3, the range of application can be broadened.

Since there is provided a level difference D of e.g. α mm between the anodes 21 and the cathodes 22, as described above,

the distance S_1 (about 1 mm) between the anodes 21 and the substrate W is shorter than the distance S_2 (about $(1+\alpha)$ mm) between the cathodes 22 and the substrate W. The level difference D is provided to make the properties, such as oxidizing or reducing properties, of the processing liquid 2 in the vicinity of the upper surface of the substrate W dependent on a gas generated at the electrodes closer to the substrate W. Since the anodes 21 are disposed closer to the substrate W than the cathodes 22 according to this embodiment, a strong oxidizing power can be imparted to the processing liquid 2 in the vicinity of the upper surface of the substrate W. In order to uniformize the properties of the processing liquid 2 over the entire upper surface of the substrate W, the anodes 21 and the cathode 22 should preferably be disposed as finely as possible.

Further, since the supply ports 25 are provided close to the substrate W, and the suction ports 29 are provided farther from the substrate W than the supply ports 25, a polymer or resist material (processing object) that has been removed from the surface of the substrate W can be prevented from again adhering to the surface of the substrate W.

A description will now be given of removal of fine particles adhering to the substrate W and cleaning of interiors of fine contact holes formed in a low-k material by the substrate processing apparatus of this embodiment.

Zeta potential, which is a factor of adsorption of particles onto the substrate W, is generally said to decrease at pH 9-10. According to this embodiment, in order to remove fine particles, an ionic surfactant is preferably used as an

additive for the processing liquid. A pulse waveform is selected as a current waveform to be applied. Further, the cathodes 22 are disposed close to the substrate W so as to impart a reducing power to the processing liquid. In addition, pH adjustment of the processing liquid is effected by adding NH_3OH as an electrolyte to the processing liquid. By such a combination, the fine particles can be enveloped in the ionic surfactant and such particles can be released from the surface of the substrate W by the action of the electric field.

An ionic chelating agent or a plating brightener may be used as an additive in the case of removing metal particles from the substrate W. In the case of removing polar organic particles, an organic adsorptive material, such as an ionic surfactant or dye agent, may be used. Thus, the ionic organic adsorptive material is allowed to be adsorbed on organic particles or an organic material, and such particles or material can be released from the surface of the substrate W by the action of the electric field.

In the case of cleaning interiors of fine contact holes formed in a low-k material, water present as a solvent of the processing liquid is electrolyzed to make the molecular structure of water finer, thereby promoting intrusion of the processing liquid into the contact holes. Especially, by using a pulse waveform as the waveform of the electric current applied between the anodes 21 and the cathodes 22, OH^- and H^+ ions having a large mobility in the processing liquid can be increased, thus further facilitating intrusion of the processing liquid into the contact holes. The increase of the mobile ions also promotes

movement of released particles in the contact holes and, together with the use of the ionic organic adsorptive material, can discharge the removal objects, present in the contact holes, out of the contact holes. The above-described O_3 can be used effectively for removal of an organic material in the fine holes.

Next, a substrate processing system incorporating a substrate processing apparatus according to the present invention will now be described in detail by referring to Fig. 9. FIG. 9 is a plan view showing the construction of the substrate processing system provided with a substrate processing apparatus according to the present invention. Though the following description relates to the construction of the system in the case of removing copper (Cu) formed in the surface of a substrate W, the system construction will be substantially the same also in the case of processing other processing objects.

As shown in FIG. 9, the substrate processing system includes a pair of loading/unloading sections 37 for carrying in and out a cassette (not shown) housing substrates W with copper as a processing object formed in the surface, four substrate processing apparatuses 1, a transfer robot 38 for transferring a substrate W, and a housing 39 that houses these devices. Transfer rails 40 are laid centrally in the housing 39, and the transfer robot 38 can move on the transfer rails 40. The substrate processing apparatuses 1 are disposed two and two on either side of the transfer rails 40, and the loading/unloading sections 37 are disposed near one end of the transfer rails 40. A substrate W is transferred between the loading/unloading section 37 and the substrate processing apparatus 1 by the

transfer robot 38.

The operation of the substrate processing system having the above construction will now be described.

The cassette housing substrates W is set in the loading/unloading section 37, and one substrate W is taken by the transfer robot 38 out of the cassette. The transfer robot 38 transfer the substrate W to the substrate processing apparatus 1, where the substrate W is held by the substrate holder 3 (see FIG. 1) of the substrate processing apparatus 1. The processing head 12 is on standby in the retreat position shown by the broken lines in FIG. 2 until the substrate W is held by the substrate holder 3. After the substrate W is held by the substrate holder 3, the processing head 12 (see FIG. 1) moves to the vicinity of the upper surface of the substrate W, where electrolytic processing (electrolytic etching) of copper on the substrate is carried out. Since the operation of the substrate processing apparatus 1 has been described previously, a description thereof is here omitted.

After completion of the electrolytic processing, the processing head 12 moves to the above-described retreat position, while the substrate W held by the substrate holder 3 is returned by the transfer robot 38 to the cassette of the loading/unloading section 37. Since the substrate processing system is provided with four substrate processing apparatuses 1, electrolytic processing of a plurality of substrates W can be performed in a continuous manner.

As described hereinabove, the present invention makes it possible to provide a positive potential to a conductive material

(processing object), formed in the surface of a substrate, through the so-called bipolar phenomenon so as to oxidize the conductive material, thereby electrically dissolving and removing the conductive material. Further, it is possible to effectively utilize the strong oxidizing power of O_3 or an active oxygen, which is generated at the anodes by electrolysis of water present as a solvent in a processing liquid, to remove an organic material, such as a polymer or a resist material. Further, a reducing atmosphere can be created according to the present invention so as to remove particles on the surface of a substrate. Furthermore, it is possible to enhance the permeability of a processing liquid into fine holes by electrolysis of the solvent and also to increase the mobility of the ions, thereby promoting intrusion of the processing liquid into the fine holes. This enables effective removal of an organic material and particles present in the fine holes.

FIG. 10 is a cross-sectional view showing the overall construction of a substrate processing apparatus according to another embodiment of the present invention. FIG. 11 is a view showing the lower surface of the processing head, and FIG. 12 is a cross-sectional view taken along the line IV-IV of FIG. 11. This embodiment differs from the above-described embodiment shown in FIGS. 1 through 4 in the following respects.

A motor 52 is fixed to the free end of the arm 11, and the motor 52 is coupled to a rotating shaft 54 of the processing head 12. By the actuation of the motor 52, the processing head 12 rotates via the rotating shaft 54 concentrically with a substrate W. The motor 52 constitutes a relative movement mechanism which

moves the processing head 12 relative to the substrate W. As shown in FIG. 11, a plurality of anodes 21 and cathodes 22, and two ultrasonic transducers 56 for emitting ultrasonic waves toward the processing liquid 2 on the substrate W are disposed in the lower surface of the processing head 12. As shown in FIG. 12, the anodes 21 are electrically connected via a wire 31 to the anode of a pulse power source 58, while the cathodes 22 are electrically connected via a wire 33 to the cathode of the pulse power source 58. The pulse power source 58 applies a pulse voltage with a predetermined frequency to the anodes 21 and the cathodes 22. The pulse voltage herein refers to a voltage (potential) that changes periodically, and not a continuous direct current voltage generally employed for electrochemical reactions.

A description will now be given of the principle of generation of microbubbles in the processing liquid by the application of a pulse voltage. As described previously, when a conductive diamond is used as a material for the anodes 21 and the cathodes 22, O_2 and O_3 are generated as gas bubbles at the anodes 21. If a direct current voltage is applied between the anodes 21 and the cathodes 22, the O_2 and O_3 gas bubbles generated at the anodes 21 inevitably grow large. Thus, microbubbles having a small diameter cannot be obtained.

In the case of applying a pulse voltage between the anodes 21 and the cathodes 22, on the other hand, the gas bubbles generated at the anodes 21 can be released from the anodes 21 before the gas bubbles grow large. It is thus possible to obtain microbubbles having a small diameter. The diameter of

microbubbles is preferably not more than 20 μm, more preferably 1 to 10 μm. In order to release the gas bubbles generated at the anodes 21 therefrom before the gas bubbles grow large, the frequency of the pulse voltage should preferably be somewhat low. That is, the pulse voltage should preferably have such a frequency that can produce microbubbles having the above diameter.

Next, a description will now be given of the ultrasonic transducers 56 provided in the substrate processing apparatus of this embodiment.

As shown in FIG. 11, the ultrasonic transducers 56 each have a fan-like shape and are disposed symmetrically about the center of the processing head 12. The ultrasonic transducers 56 are connected to a not-shown power source, and a high-frequency alternating current voltage is applied from the power source to the ultrasonic transducers 56. The ultrasonic transducers 56 convert the periodical electrical signal from the power source into a mechanical vibration, thus generating an ultrasonic vibration. An electrostriction transducer as typified by barium titanate or lead zirconate titanate, or a magnetostriction transducer as typified by ferrite, is preferably used as the ultrasonic transducer 56.

The ultrasonic transducers 56 are disposed adjacent to the area in which the anodes 21 and the cathodes 22 are disposed. When the processing liquid 2 is supplied from the supply ports 25 (see FIG. 12) onto the substrate W while rotating the processing head 12 by the motor 52 (see FIG. 10), the processing liquid 2 spreads over the entire surface of the substrate W due to the rotation of the processing head 12. Ultrasonic waves are

then emitted from the ultrasonic transducers 56 toward the processing liquid 2 that fills the space between the substrate W and the processing head 12. As described above, microbubbles of O_2 and O_3 remain in the processing liquid 2, and the ultrasonic waves from the ultrasonic transducers 56 are applied to the microbubbles.

When ultrasonic waves are applied to the microbubbles, the microbubbles are stirred by the energy of the ultrasonic waves and diffuse throughout the processing liquid. Part of the microbubbles are collapsed by the application of ultrasonic waves, whereby micro jet flows are created in the processing liquid 2. Particles, etc. adhering to the substrate W are removed by the physical energy of the micro jet flows. Further, when the microbubbles are collapsed, the O_2 or O_3 forming the microbubbles is dissolved at a high concentration in the processing liquid. Especially, the high-concentration O_3 has a strong oxidizing power. By utilizing the oxidizing power, an organic material, such as a resist material or a polymer, on the substrate W can be removed.

Further, the microbubbles floating in the processing liquid, without being collapsed, can be utilized to remove particles floating in the processing liquid and particles remaining on the substrate W. Thus, by utilizing the electrical charge of the microbubbles, particles can be adsorbed on the surfaces of the microbubbles and removed. Further, since the ultrasonic waves are reflected diffusely on the surfaces of the microbubbles, the ultrasonic waves can be applied to a fine processing portion (device) formed in the substrate W. Thus,

according to the substrate processing apparatus of this embodiment, various processing objects, such as particles, a metal and an organic material, can be removed from the substrate W with a high efficiency by the combination of the cleaning effect of electrolytic processing, the cleaning effect of microbubbles and the cleaning effect of ultrasonic waves.

After completion of the series of cleaning processings, the processing head 12 is rotated at a high speed, whereby the processing liquid adhering to the processing head 12 can be removed by centrifugal action. During cleaning, it is preferred to pivot the processing head 12 while rotating it. By thus moving the processing head 12 relative to the substrate W, ultrasonic waves can be applied also to the center of the substrate W, enabling uniform processing over the entire substrate W. In this case, the motor 14, the arm 11 and the power transmission mechanism 13 for pivoting the processing head 12, together with the motor 52 for rotating the processing head 12, constitute a relative movement mechanism. The processing head 12 may be reciprocated over the substrate W.

The frequency of the ultrasonic waves emitted from the ultrasonic transducer 56 is preferably not less than 5 MHz and not more than 100 MHz, more preferably not less than 10 MHz and not more than 50 MHz. There is a likelihood that as devices become finer in the future, ultrasonic waves within a frequency band of 1 to 5 MHz may cause damage to a device. On the other hand, ultrasonic waves within a frequency band of 10 to 50 MHz are unlikely to cause damage to a device formed in a substrate W. Ultrasonic waves having a frequency over 100 MHz have a poor

energy to move the microbubbles in the processing liquid. The use of such ultrasonic waves, therefore, lowers the cleaning effect. For the above reasons, the frequency of ultrasonic waves is set at 5 to 100 MHz, preferably 10 to 50 MHz.

According to the present invention, various processing objects, such as particles, a metal and an organic material, can be removed from a substrate with a high efficiency by the combination of the cleaning effect of electrolytic processing, the cleaning effect of microbubbles and the cleaning effect of ultrasonic waves.

FIG. 13 is a cross-sectional view showing the overall construction of a substrate processing apparatus according to yet another embodiment of the present invention. This embodiment differs from the above-described embodiment shown in FIGS. 1 through 4 in the following respects.

A motor 62 is coupled via a power transmission mechanism 60 to the lower end of the main shaft 4 according to this embodiment. With such a construction, a substrate W held by the substrate holder 3 rotates via the main shaft 4 by the actuation of the motor 62. The motor 62 constitute a rotating mechanism for rotating the substrate holder 3 and the substrate W. The processing head 12 has a circular horizontal cross-section with approximately the same diameter as the substrate W. The processing head 12 has an ultrasonic transducer 64 mounted to the lower surface thereof. The ultrasonic transducer 64, as with the processing head 12, has a circular horizontal cross-sectional and is disposed such that it faces the substrate W held by the substrate holder 3.

A processing liquid introduction port 66 for introducing a processing liquid 2 to the substrate W is formed in the center of the processing head 12. The processing liquid introduction port 66 is open in the center of the ultrasonic transducer 64. The processing liquid introduction port 66 communicates with a through-hole 70 provided in a support shaft 68 and the arm 11, and the through-hole 70 in turn communicates via a pipe 72 to a processing liquid supply source 74 in which the processing liquid 2 is stored. With such construction, the processing liquid 2 stored in the processing liquid supply source 74 is supplied through the pipe 72, the through-hole 70 and the processing liquid introduction port 66 onto the substrate W.

A microbubble generator 76 for generating microbubbles in the processing liquid 2 is housed in the processing liquid supply source 74. The microbubble generator 76 is designed to generate microbubbles having a diameter of not more than 20 μm, preferably 1 to 10 μm, and an internal pressure of not lower than atmospheric pressure. Specific examples of the microbubble generator 76 are as follows:

(1) Two-fluid nozzle

The two-fluid nozzle has a liquid introduction hole that is open in a mixing chamber, and a gas introduction hole adjacent to the liquid introduction hole. A pressurized liquid (processing liquid) is jetted vigorously from the liquid introduction hole into the mixing chamber. Due to a negative pressure produced by the fluid energy of the jetted liquid, a gas is introduced by suction from the gas introduction hole into the mixing chamber. The gas is mixed into the flow of the liquid,

whereby a gas/liquid mixed flow containing microbubbles is formed.

(2) Gas diffuser with a porous material

A porous material, such as an air stone, has a large number of small pores communicating with each other, and part of the pores are open in the surface of the porous material. When a gas is introduced into the porous material which is immersed in a liquid, the gas posses through the small pores and is discharged as fine bubbles from the surface of the porous material into the liquid. It is, therefore, possible to generate microbubbles having a desired diameter by using an appropriate small pore diameter. A membranous gas diffusing material may also be used as the porous material.

(3) Gas/liquid stirrer

The gas/liquid stirrer includes a stirring member, such as a screw, disposed in a liquid, and rotates the stirring member at a high speed while supplying a gas into the liquid, thereby stirring the gas present as gas bubbles in the liquid. As a result, the gas bubbles in the liquid are made finer and become microbubbles.

The microbubble generator 76 is connected to a gas supply source 78, and microbubbles are generated with the microbubble generator 76 using a gas supplied from the gas supply source 78. According to this embodiment, ozone (O_3), oxygen difluoride (F_2O), carbon dioxide (CO_2), a mixed gas of ozone and carbon dioxide, etc. are preferably used as the gas for forming microbubbles. The gas may be appropriately selected depending upon the type of the material to be processed.

For example, ozone is used for removal of an organic material, such as a polymer or a resist material. Ozone has a strong oxidizing power and can decompose the organic material into CO_2, etc., thereby removing the organic material. Oxygen difluoride is used for removal of an unnecessary metal, such as Cu or Al, remaining on the substrate W. Oxygen difluoride has a strong oxidizing power and can dissolve and remove the metal, such as Cu or Al. Ozone can be used also for removal of a metal.

A mixed gas of ozone and carbon dioxide is used for removal of a polymer adhering to a device portion (fine processing portion) formed in the surface of the substrate W. A processing liquid, in which carbon dioxide is mixed, can be used as a post-polishing rinsing liquid. The pressing liquid containing carbon dioxide, as compared to a pure water rinsing liquid, can prevent the generation of static electricity. Accordingly, the processing liquid can prevent the device portion formed in the substrate W from being electrically charged.

Next, the operation of the substrate processing apparatus having the above construction will now be described.

First, the motor 14 is driven to move the processing head 12 to a position above the substrate W held by the substrate holder 3. The processing head 12 is then moved downwardly by the air cylinder 16 to thereby bring the ultrasonic transducer 64 close to the surface of the substrate W. At this time, the microbubble generator 76 is driven to generate microbubbles in the processing liquid 2 stored in the processing liquid supply source 74.

Next, the motor 62 is driven to rotate the substrate W while the processing liquid 2 containing microbubbles is supplied from

the processing liquid supply source 74 and through the processing liquid introduction port 66 onto the substrate W. Due to the rotation of the substrate W, the processing liquid 2 spreads radially and outwardly on the substrate W and finally flows out of the peripheral end of the substrate W. The processing liquid 2 which has flowed out of the substrate W is recovered in the vessel 5. Ultrasonic waves are emitted from the ultrasonic transducer 64 toward the processing liquid 2 present between the substrate W and the ultrasonic transducer 64.

When the ultrasonic waves are applied to the microbubbles, the microbubbles are stirred and diffuse throughout the processing liquid 2. Part of the microbubbles are collapsed by the application of ultrasonic waves, whereby micro jet flows are formed in the processing liquid 2. A processing object adhering to the substrate W can be removed by utilizing the physical energy of the micro jet flows. When the microbubbles are collapsed, the gas forming the microbubbles, such as ozone, dissolves at a high concentration in the processing liquid 2. A processing object on the substrate W can be removed by utilizing the chemical properties of the gas.

Microbubbles floating in the processing liquid 2, without being collapsed, can be utilized to remove particles floating in the processing liquid 2 and particles remaining on the substrate W. Thus, by utilizing the electrical charge of the microbubbles, particles can be adsorbed on the surfaces of the microbubbles and removed. Further, since the ultrasonic waves are reflected diffusely on the surfaces of the microbubbles, the ultrasonic waves can be applied to a fine processing portion

(device) formed in the substrate W. Thus, according to the substrate processing apparatus of this embodiment, various processing objects, such as particles, a metal and an organic material, can be removed from the substrate W with a high efficiency by the combination of the cleaning effect of microbubbles and the cleaning effect of ultrasonic waves.

As with the preceding embodiment, the frequency of the ultrasonic waves emitted from the ultrasonic transducer 64 is set at 5 to 100 MHz, preferably 10 to 50 MHz.

Though in this embodiment the processing liquid 2 containing microbubbles is supplied to the substrate W, it is also possible to supply the processing liquid 2 not containing microbubbles to the substrate W, and then generate microbubbles of ozone by electrolysis in the processing liquid. In this case, a conductive diamond or lead dioxide (PbO_2) is preferably used for an anode. Further, in order to make the diameter of gas bubbles smaller, a surfactant is mixed in the processing liquid, or a pulse voltage is applied between an anode and a cathode.

It is also possible to provide a drying device to the substrate processing apparatus and carry out drying subsequently to the cleaning processing. For example, the main shaft 4 (see FIG. 13) may be rotated at a high speed after the cleaning processing for centrifugal drying of the substrate W on the substrate holder 3. It is possible to carry out rinsing processing between the cleaning processing and drying to remove the processing liquid which adhered to the substrate W during the cleaning processing. For example, a rinsing liquid, such as ultrapure water, may be supplied from the processing liquid

introduction port 66 (see FIG. 13) onto the substrate W, thereby replacing the processing liquid adhering to the substrate W with the rinsing liquid. It is preferred, also in the rinsing processing, to generate microbubbles in the rinsing liquid and apply ultrasonic waves to the rinsing liquid. Further, through in this embodiment only the front surface (upper surface) of the substrate W is subjected to the cleaning processing, it is also possible to provide a processing liquid introduction port, an ultrasonic transducer, etc. also on the back surface (lower surface) side of the substrate W so as to clean not only the front surface but also the back surface of the substrate W. Also in this case, the rinsing processing may be carried out after the cleaning processing. Further, the drying may be carried out between the cleaning processing and the rinsing processing.

According to the present invention, various processing objects, such as particles, a metal and an organic material, can be removed from a substrate with a high efficiency by the combination of the cleaning effect of microbubbles and the cleaning effect of ultrasonic waves.

FIG. 14 shows a substrate processing apparatus, which is utilized as an etching apparatus, according to yet another embodiment of the present invention. The substrate processing apparatus (etching apparatus) includes a substrate holder 210 for detachably holding and rotating a substrate W with its processing surface facing downwardly. The substrate holder 210 includes a circular substrate stage 212 and a plurality of support pins 214 mounted vertically on the peripheral portion of the substrate stage 212. Each support pin 214 has at the top end

a gripper (not shown), such as a chucking claw, for detachably holding the substrate W by gripping the peripheral portion of the substrate W.

The substrate stage 212 is coupled to the upper end of a hollow main shaft 216. The main shaft 216 is designed to rotate by a first drive mechanism 226 which includes a driven pulley 218 mounted to the lower end of the main shaft 216, a driving pulley 222 mounted to a motor 220, and a timing belt 224 extending between the pulleys 218, 222. By the actuation of the motor 220 of the first drive mechanism 226, the substrate holder 210 holding the substrate W rotates together with the substrate W.

Positioned slightly below the substrate W held by the substrate holder 210, a circular rotary plate 230 having a slightly smaller diameter than the substrate W is disposed parallel to the substrate W. Thus, a first processing space 232 with a distance A is formed between the lower surface (processing surface) of the substrate W held by the substrate holder 210 and the upper surface of the rotary plate 230. The rotary plate 230 is coupled to the upper end of a rotating shaft 234 extending inside the main shaft 216. The rotating shaft 234 is designed to rotate by a second drive mechanism 244 which includes a driven pulley 236 mounted to the lower end of the rotating shaft 234, a driving pulley 240 mounted to a motor 238, and a timing belt 242 extending between the pulleys 236, 240.

The distance A between the substrate W and the rotary plate 230 may be set arbitrarily depending upon the amount of processing fluid supplied to the first processing space 232 so that the first processing space 232 is filled with the processing fluid.

In the central portion of the rotating shaft 234, a through-hole 234a, extending in the axial direction and vertically penetrating the rotating shaft 234, is provided as a first fluid supply section for introducing an etching liquid (first processing fluid) Q supplied from an etching liquid supply source 235 into the first processing space 232.

Positioned above the substrate holder 210 is disposed a counter plate 284 which is vertically movable and extends downwardly in the peripheral portion and which, when lowered, surrounds the upper surface and the side of the substrate W held by the substrate holder 210 and forms a second processing space 246 with a distance B between it and the substrate W held by the substrate holder 210.

In the center of the counter plate 248, a through-hole 248a vertically penetrating the counter plate 248 is provided as a second fluid supply section for introducing air (second processing fluid) supplied from an air supply source 249 into the second processing space 246.

Next, a description will now be given of etching processing carried out by this etching apparatus.

First, when the counter plate 248 is in a raised position, a substrate W is held by the support pins 214 of the substrate holder 210. Thereafter, the counter plate 248 is lowered to a predetermined position. The first drive mechanism 226 is driven to rotate the substrate W together with the substrate holder 210 and, at the same time, the second drive mechanism 244 is driven to rotate the rotary plate 230. The substrate W and the rotary plate 230 are preferably rotated in opposite directions so as

to increase the relative movement speed between the substrate W and the rotary plate 230. This enhances uniformity of the diffusion layer on the processing surface of the substrate W. From the viewpoint of preventing damage to the substrate W, it is preferred to use a low rotational speed for the substrate W and a high rotational speed for the rotary plate 230. In the case of rotating the substrate W and the rotary plate 230 in the same direction, their rotational speeds should be made different so as to produce a relative movement speed between them.

While thus rotating the substrate W and the rotary plate 230 preferably in opposite directions, the etching liquid Q, for example DHF in the case of etching of SiN, is passed through the through-hole 234a provided centrally in the rotating shaft 234 and jetted toward the processing surface (lower surface) of the rotating substrate W held by the substrate holder 210, thereby introducing the etching liquid Q into the first processing space 232 formed between the substrate W and the rotary plate 230.

By thus jetting the etching liquid Q toward the rotating substrate W held by the substrate holder 210, etching can be carried out, in principle, in a spin-etching manner. Further, by filling the first processing space 232, formed between the substrate W held by the substrate holder 210 and the rotary plate 230, with the etching liquid Q and causing the etching liquid Q, which has passed through the first processing space 232, to scatter out by centrifugal force from the peripheral end of the substrate W, as shown in FIG. 15A, contact between air and the surface of the etching liquid Q in the first processing space 232 can be prevented as much as possible, thereby preventing the

liquid surface from becoming wavy. This prevents uneven etching in the peripheral region of the substrate W even when the substrate W is rotated at a high speed. Further, by rotating the substrate W and the rotary plate 230 in such a manner that a relative movement speed is produced between them, the effect of rotation of the substrate W produced in immersion wet etching can be produced also in the spin etching, thereby enhancing the uniformity of etching processing of the substrate W.

Simultaneously with the above operation, air (dry air) is introduced through the through-hole 248a provided in the counter plate 248 into the second processing space 246 formed between the non-processing surface (upper surface) of the substrate W held by the substrate holder 210 and the counter plate 248, and the air is caused to flow along the non-processing surface (upper surface) toward the periphery of the substrate W. This prevents the etching liquid Q from intruding over the peripheral end surface into the non-processing surface (upper surface) of the substrate W.

It is not always necessary that the first processing space 232, formed between the substrate W and the rotary plate 230, be completely filled with a processing fluid such as the etching liquid Q. As shown in FIG. 15B, even if an air-intrusion space S is formed in a portion, corresponding to a peripheral portion of the substrate W, of the etching liquid Q, waving of the surface of the etching liquid Q can be avoided and uneven etching can be prevented, provided the pressure in the air-intrusion space S is lower than atmospheric pressure.

After completion of the etching, the supply of the etching

liquid Q into the first processing space 232 and the supply of air into the second processing space 246 are stopped, and then the rotation of the substrate W and the rotation of the rotary plate 230 are stopped, and the rotary plate 248 is raised. Thereafter, the substrate W after etching is taken, for example, by a robot hand from the support pins 214 of the substrate holder 210, and sent to the next process step.

Though in this embodiment air (dry air) is introduced into the second processing space 246 formed between the substrate W and the counter plate 248, it is also possible to introduce an etching liquid into the second processing space 246. Thus, an etching liquid may be jetted also onto the upper surface of the rotating substrate W held by the substrate holder 210 so as to carry out etching of both the front and back surfaces of the substrate W simultaneously.

FIG. 16 shows a substrate processing apparatus, which is utilized as an etching apparatus, according to yet another embodiment of the present invention. This embodiment differs from the embodiment shown in FIG. 15 in the following respects. The second processing space 246 is formed between the substrate W held by the substrate holder 210 and a disk-like counter plate 248 having approximately the same size as the substrate W. The counter plate 248 is coupled to the lower end of a second rotating shaft 260 which is designed to rotate by a third drive mechanism 258 which includes a driven pulley 250 mounted to the upper end of the second rotating shaft 260, a driving pulley 254 mounted to a motor 252, and a timing belt 256 extending between the pulleys 250, 254. Further, in the central portion of the second rotating

shaft 260 is provided a through-hole 260a, extending in the axial direction and vertically penetrating the second rotating shaft 260, as a second fluid supply section for introducing an etching liquid (second processing fluid) supplied from a second etching liquid supply source 262 into the second processing space 246. The other construction is the same as the embodiment shown in FIG. 14.

According to this embodiment, as with the preceding embodiment, while rotating the substrate W and the rotary plate 230 preferably in opposite directions, an etching liquid (first processing fluid) is passed through the through-hole 234a provided centrally in the rotating shaft 234 and jetted toward one processing surface (lower surface) of the rotating substrate W held by the substrate holder 210 to carry out etching of the processing surface (lower surface); at the same time, while rotating the counter plate 248 preferably in a direction opposite to the rotating direction of the substrate W, an etching liquid (second processing fluid) is passed through the through-hole 260a provided centrally in the second rotating shaft 260 and jetted toward the other processing surface (upper surface) of the rotating substrate W held by the substrate holder 210 to carry out etching of the processing surface (upper surface). Simultaneous etching of both the front and back surfaces of the substrate W can thus be carried out with enhanced uniformity of etching over the entire processing surfaces.

The optimum rotating directions and rotational speeds of the substrate W, the rotary plate 230 and the counter plate 248 respectively in the etching, rinsing and drying steps may be

determined depending upon the respective processing conditions.

This embodiment is useful especially in a case where simultaneous etching of both the front and back surfaces of a substrate W is necessary and a high level of etching uniformity is required for the both surfaces. In particular, the rotational speeds of the rotary plate 230 and the counter plate 248 may preferably be controlled independently, whereby the relative rotational speeds between them and the rotating substrate W held by the substrate holder 210 can be optimized.

FIG. 17 shows a substrate processing apparatus, which is utilized as an etching apparatus, according to yet another embodiment of the present invention. This embodiment differs from the embodiment shown in FIG. 14 in the following respects. The substrate holder 210 holds and rotates a substrate W with its processing surface facing upwardly. The rotary plate 230, which is rotatable by the second drive mechanism 244, is disposed above the substrate W held by the substrate holder 210, so that the first processing space 232 is formed between the substrate W and the rotary plate 230 on the upper surface side of the substrate W. Further, a disk-like counter plate 248 is disposed below the substrate W held by the substrate holder 210, so that the second processing space 246 is formed between the substrate W and the counter plate 248 on the lower surface side of the substrate W. The counter plate 248 is coupled to the upper end of a fixed shaft 264. Inside the fixed shaft 246 is provided a through-hole 264a, vertically extending and penetrating the fixed shaft 264, as the second fluid supply section for introducing air (second processing fluid) supplied from the air

supply source 249 into the second processing space 246. The other construction is the same as that shown in FIG. 14. Further, etching processing is also carried out in the same manner, and hence a description thereof is omitted.

According to this embodiment, etching of the processing surface (upper surface) of a substrate W is carried out while the substrate is held with the processing surface facing upwardly. This makes it possible, for example, to hand over a substrate, which has been transferred with its processing surface facing upwardly, directly to the substrate holder 210, i.e. without 180°-rotating the substrate, to carry out etching of the substrate.

FIG. 18 is a schematic plan view showing a substrate processing system provided with an etching apparatus (substrate processing apparatus) as described above. As shown in Fig. 18, the substrate processing system includes two substrate cassettes 151a, 151b for housing substrates W, the etching apparatus (substrate processing apparatus) 152 for etching a substrate W, a substrate cleaning apparatus 153 for cleaning the substrate W after etching, and a substrate drying apparatus 154 for drying the substrate W after cleaning. The substrate processing system also includes a first transfer robot 155a and a second transfer robot 155b for transferring the substrate W between the above apparatuses, and a buffer stage 156 for temporarily placing the substrate W thereon.

The substrate cassettes 151a, 151b are each provided with a plurality of cabinets (not shown) for housing substrates W, and one substrate W as a processing object is housed in each

cabinet. The substrates W housed in the substrate cassettes 151a, 151b are taken out, one by one, by the first transfer robot 155a, and each substrate W is handed over to the second transfer robot 155b via the buffer stage 156. The substrate W is then transferred by the second transfer robot 155b to the etching apparatus 152, where the substrate W is held by the substrate holder 210 (see, for example, FIG. 14) and etching of the substrate W is carried out.

When copper adhering to or formed on the substrate W, for example, is the etching object in the etching processing, a combination of an acid solution and an oxidizing agent solution may preferably be used as an etching solution. Any non-oxidative acid may be used as the acid solution, and examples include hydrofluoric acid, hydrochloric acid, sulfuric acid, citric acid, oxalic acid, nitric acid, and a mixed solution thereof. Examples of the oxidizing agent solution include ozone water, a hydrogen peroxide solution, a nitric acid solution, and a sodium hypochlorite solution. Hydrofluoric acid, for example, may be used as an etching liquid for etching of a SiO_2 film. A mixed solution of hydrofluoric acid and hydrochloric acid, for example, may be used as an etching liquid for etching of a SiN film. Further, a mixed solution of hydrofluoric acid and nitric acid, for example, may be used for etching of a poly-silicon film. For a pre-electroless plating processing, sulfuric acid, citric acid, oxalic acid, TMAH, NH_4OH, or the like may be used.

After the etching processing in the etching apparatus 152, the substrate W is carried by the second transfer robot 155b into the substrate cleaning apparatus 153. The substrate cleaning

apparatus 153 is provided with a roll sponge (not shown) for cleaning the substrate W and is designed to clean a substrate by bringing the roll sponge into contact with the substrate while holding and rotating the substrate. A product produced by the etching processing, etc. can be cleaned off by the substrate cleaning apparatus 153. The substrate W after cleaning is transferred by the second transfer robot 155b from the substrate cleaning apparatus 153 to the substrate drying apparatus 154. The substrate drying apparatus 154 includes a spin-drying section (not shown) for rotating the substrate W at a high speed so as to dry the substrate W. A cleaning liquid, etc. adhering to the substrate W can be dried off by the spin-drying section. The substrate W after drying is transferred by the first transfer robot 155a and returned to the substrate cassette 151a or 151b, to thereby complete the series of process steps.

As described hereinabove, the substrate processing apparatus of the present invention, in principle, performs spin processing by supplying the first processing fluid, such as an etching liquid, from the first fluid supply section to a rotating substrate held by the substrate holder. By holding the processing fluid, supplied from the first fluid supply section, between the substrate held by the substrate holder and the rotary plate and preventing contact between the processing fluid and air as much as possible, uneven processing in the peripheral region of the substrate can be avoided even when the rotational speed of the substrate is high. Further, by producing the effect of rotation of substrate in immersion processing also in the spin processing, uniformity of processing, such as etching, of the substrate can be enhanced.